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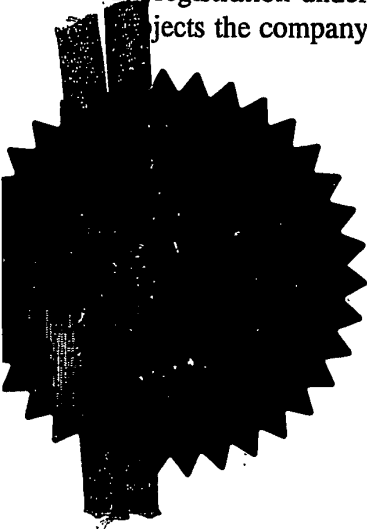
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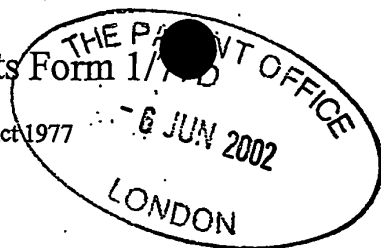
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Signed *Stephen Hordley*  
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## Request for grant of a patent

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1.	Your reference	8397 GB / SMS		
2.	Patent application number (The Patent Office will fill in this part)	06 JUN 2002 0212977.3		
3.	Full name, address and postcode of the or of each applicant ( <i>underline all surnames</i> )	Vantico AG Klybeckstrasse 200 4057 Basle Switzerland		
	Patents ADP number ( <i>if you know it</i> )	08016990001		
	If the applicant is a corporate body, give the country/state of its incorporation	Switzerland		
4.	Title of the invention	Actinic Radiation Curable Compositions and their Use		
5.	Name of your agent ( <i>if you have one</i> ) "Address for service" in the United Kingdom to which all correspondence should be sent ( <i>including the postcode</i> )	Abel & Imray 20 Red Lion Street London WC1R 4PQ		
	Patents ADP number ( <i>if you know it</i> )	174001 ✓		
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and ( <i>if you know it</i> ) the or each application number	Country	Priority application number ( <i>if you know it</i> )	Date of filing ( <i>day/month/year</i> )
7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing ( <i>day/month/year</i> )	
8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? ( <i>Answer 'Yes' if:</i> <i>a) any applicant named in part 3 is not an</i> <i>inventor, or</i> <i>b) there is an inventor who is not named as an</i> <i>applicant, or</i> <i>c) any named applicant is a corporate body.</i>	YES		

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Description 32

Claim(s) 6

Abstract 1

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10. If you are also filing any of the following, state how many against each item.

Priority documents

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*) One

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11. I/We request the grant of a patent on the basis of this application.

Signature

Date

*Abel & Imray*

06 June 2002

Abel & Imray

12. Name and daytime telephone number of person to contact in the United Kingdom  
Susan M Scott  
020 7242 9984

Actinic Radiation Curable Compositions and their Use

The present invention relates to actinic radiation  
5 curable compositions and their use.

Curable compositions containing epoxy resins are very  
well known. Many are heat curable. For example, US  
patents 4,341,819, 5,688,878, 5,780,560, 5,932,288 and  
6,316,049 describe heat curable compositions containing an  
10 epoxy together with a crosslinking agent of the  
methylenedisalicylic acid type. The cure catalyst in US  
6,316,049 may be a  $\text{BF}_3$ :amine complex in which the amine is  
primary, secondary, or tertiary and has a boiling point of  
about 106°C or below.

15 Actinic radiation curable liquid resins or resin  
mixtures are very versatile. For example, they can be  
used as coating compositions, adhesives or photoresists.  
They may also be used for the manufacture of three-  
dimensional objects using stereolithography. In this  
20 technique the desired shaped article is built up from a  
liquid, radiation-curable composition with the aid of a  
recurring, alternating sequence of two steps (a) and (b);  
in step (a), a layer of the liquid, radiation-curable  
composition, one boundary of which is the surface of the  
25 composition, is cured with the aid of appropriate  
radiation, generally radiation produced by a preferably  
computer-controlled laser source, within a surface region  
which corresponds to the desired cross-sectional area of  
the shaped article to be formed, at the height of this  
30 layer, and in step (b) the cured layer is covered with a  
new layer of the liquid, radiation-curable composition,  
and the sequence of steps (a) and (b) is repeated until a  
so-called green model of the desired shape is finished.

This green model is, in general, not yet fully cured and must therefore, normally, be subjected to post-curing.

Much work has been put into developing suitable actinic radiation-curable compositions for the uses mentioned above. For example US 5476748 describes a novel photosensitive composition comprising an epoxy resin and a cationic photoinitiator therefor together with a cycloaliphatic or aromatic diacrylate and a radical photoinitiator therefor, and a OH-terminated polyether, polyester or polyurethane.

A major problem with actinic radiation curable compositions is that they tend to have low storage stability. Such compositions generally contain a component whose purpose is to initiate curing in the presence of radiation, and this component may be unstable under storage conditions. In such a case, small concentrations of certain species, typically photoacids, can cause the composition to discolour and to gel even if kept under cool dark conditions. Thus, EP 153904A, EP 35969A, EP 44272A, EP 54509A, EP 164314A and US 3708296 describe onium salts which may be used as initiators for radiation curable epoxy compositions. These salts are highly effective initiators. However, they have the disadvantage that they can break down on storage to produce small quantities of the corresponding acids which can initiate the curing of the epoxy compound present in the composition. This in turn leads to an increase in viscosity of the composition, and can cause gellation or even actual hardening of the composition in a relatively short period of time.

US 5665792 discloses stabilisers for photohardenable epoxy compositions, which have limited solubility in the composition and a density which is different from that of the composition.

Group IIA metal ion and a weak acid, the weak acid having a pKa in water of greater than 3.0.

There is a need for stabilizers which will increase the shelf life of actinic radiation curable epoxy compositions without adversely affecting the properties of the compositions, particularly now as new means of dispensing actinic radiation curable compositions are becoming available, for example, piezo ink jet printing.

It is known that certain complexes of boron-containing compounds with amines can be used in epoxy compositions as curing agents. US 6242513 discloses epoxy-containing compositions and at least one Lewis acid catalyst. Amongst the materials listed as suitable catalysts are borane-amine complexes and amino complexes of boron halides. The catalyst is preferably present in the composition in an amount of from 0.4% to about 0.8% by weight. US 6191681 describes an electrically conductive composite material including an epoxy together with a Lewis acid catalyst, such as a boron trichloride- or boron trifluoride-amine complex. The complex is used in an amount of about 4% by weight based on epoxy. In all these cases, the boron-amine complex is used as a catalyst, its objective being to initiate curing of the epoxy, and in order to carry out this function it is present in significant amounts.

It has now been found that certain boron-amine complexes used in much smaller amounts than previously, can act as stabilizers for epoxy compounds and other cationically polymerisable compounds in actinic radiation-curable compositions also containing an onium compound. The fact that they can act as stabilisers, i.e. that they prevent premature curing of the cationically curable compound, is most surprising in view of their well-known use as curing initiators for epoxies.

The invention therefore provides an actinic radiation curable composition comprising:

- (A) at least one actinic radiation curable, cationically polymerisable compound;
- 5 (B) at least one cationic photoinitiator for component (A); and
- (C) at least one stabiliser which is a complex of a Lewis acid and a Lewis base, component (C) being present in the composition in an amount of from 0.001 to 0.3
- 10 wt%.

Any actinic radiation curable, cationically polymerisable compound may be present in component (A) of a composition according to the invention. Epoxy compounds are preferred, and such epoxy compounds may have an

15 aliphatic, aromatic, cycloaliphatic, araliphatic or heterocyclic structure; they may comprise epoxy groups as side groups, or those groups form part of an alicyclic or heterocyclic ring system. Preferred epoxies are those having an epoxy functionality of greater than or equal to

20 2.

There may be mentioned as examples of epoxy resins of the type:

(I) Polyglycidyl and poly( $\beta$ -methylglycidyl) esters obtainable by the reaction of a compound having at least

25 two carboxy groups in the molecule and epichlorohydrin or glycerol dichlorohydrin or  $\beta$ -methyl-epichlorohydrin. The reaction is advantageously effected in the presence of

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bases.

Aliphatic polycarboxylic acids can be used as

30 compounds having at least two carboxy groups in the molecule. Examples of those polycarboxylic acids are glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid or dimerised linoleic acid.

It is, however, also possible to use cycloaliphatic poly carboxylic acids, such as, for example, tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid or 4-methylhexahydrophthalic acid.

5 It is also possible to use aromatic polycarboxylic acids, such as, for example, phthalic acid, isophthalic acid, trimellitic acid or pyromellitic acid.

It is likewise possible to use carboxy-terminated adducts, for example of trimellitic acid and polyols, such  
10 as, for example, glycerol or 2,2-bis(4-hydroxycyclohexyl)propane.

II) Polyglycidyl or poly( $\beta$ -methylglycidyl) ethers obtainable by the reaction of a compound having at least two free alcoholic hydroxy groups and/or phenolic hydroxy  
15 groups and a suitably substituted epichlorohydrin under alkaline conditions, or in the presence of an acidic catalyst with subsequent alkali treatment. Ethers of that type are derived, for example, from acyclic alcohols, such as ethylene glycol, diethylene glycol and higher  
20 poly(oxyethylene) glycols, propane-1,2-diol, or poly(oxypropylene) glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane 1,6-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, bistrimethylolpropane,  
25 pentaerythritol, sorbitol, and also from polyepichlorohydrins.

They are, however, also derived, for example, from cycloaliphatic alcohols, such as 1,3- or 1,4-dihydroxycyclohexane, bis(4-hydroxycyclohexyl)methane,  
30 2,2-bis(4-hydroxycyclohexyl)propane or 1,1-bis(hydroxymethyl)cyclohex-3-ene, or they possess aromatic nuclei, such as N,N-bis(2-hydroxyethyl)aniline or p,p-bis(2-hydroxyethylamino)diphenylmethane.



The epoxy compounds may also be derived from mononuclear phenols, such as, for example, from resorcinol or hydroquinone, or they are based on polynuclear phenols, such as, for example, bis-(4-hydroxyphenyl)methane (bisphenol F), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), or on condensation products, obtained under acidic conditions, of phenols or cresols with formaldehyde, such as phenol novolaks and cresol novolaks.

(III) Poly(N-glycidyl) compounds are, for example, obtainable by dehydrochlorination of the reaction products of epichlorohydrin with amines that comprise at least two amine hydrogen atoms. Those amines are, for example, n-butylamine, aniline, toluidine, m-xylylene diamine, bis(4-aminophenyl)methane or bis(4-methylaminophenyl)methane.

The poly(N-glycidyl) compounds also include, however, N,N-diglycidyl derivatives of cycloalkyleneureas, such as ethyleneurea or 1,3-propyleneurea, and N,N'-diglycidyl derivatives of hydantoins, such as of 5,5-dimethylhydantoin.

IV) Examples of poly(S-glycidyl) compounds are diglycidyl derivatives which are derived from dithiols, such as, for example, ethane-1,2-dithiol or bis(4-mercaptomethylphenyl) ether.

V) Examples of epoxy compounds in which the epoxy groups form part of an alicyclic or heterocyclic ring system are bis(2,3-epoxycyclopentyl) ether, 2,3-epoxycyclopentyl glycidyl ether, 1,2-bis(2,3-epoxycyclopentyloxy)ethane, bis(4-hydroxycyclohexyl)methane diglycidyl ether, 2,2-bis(4-hydroxycyclohexyl)propane diglycidyl ether, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane, 3,4-epoxy-6-methyl-cyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate, di-(3,4-epoxycyclohexylmethyl) hexanediolate, di-(3,4-epoxy-6-methyl-2-oxocyclohexanecarboxylate).

carboxylate), ethanediol di-(3,4-epoxycyclohexylmethyl) ether, vinylcyclohexene dioxide, dicyclopentadiene diepoxide or 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-1,3-dioxane.

- 5 It is, however, also possible to use epoxy resins in which the 1,2-epoxy groups are bonded to different hetero atoms or functional groups. Those compounds include, for example, the N,N,O-triglycidyl derivative of 4-aminophenol, the glycidyl ether glycidyl ester of  
10 salicylic acid, N-glycidyl-N' (2-glycidyloxypropyl)-5,5-dimethylhydantoin or 2 -glycidyloxy-1,3-bis(5,5-dimethyl-1-glycidylhydantoin-3-yl)propane.

Especially preferred are compositions containing a cycloaliphatic diepoxide, for example bis(4-hydroxycyclo-  
15 hexyl)methane diglycidyl ether, 2,2-bis(4-hydroxycyclohexyl)propane diglycidyl ether, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4 -epoxy-6-methyl-cyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate, di-(3,4-epoxycyclohexylmethyl)hexanedioate, di-(3,4-epoxy-  
20 6-methyl-cyclohexylmethyl)hexanedioate, ethylenebis(3,4-epoxycyclohexanecarboxylate), ethanediol di-(3,4-epoxy-cyclohexylmethyl) ether or 2-(3,4-epoxycyclohexyl)-5,5,3-dioxane. The monomer purity of any cycloaliphatic diepoxide is preferably 90% or higher.

- 25 Curable commercial epoxy products that can be used herein include: Uvacure 1500, Uvacure 1501, Uvacure 1502, Uvacure 1530, Uvacure 1531, Uvacure 1532, Uvacure 1533, Uvacure 1534, Uvacure 1561, Uvacure 1562, all commercial products of UCB Radcure Corp., Smyrna, GA; UVR-6105, UVR-  
30 6100, UVR-6110, UVR-6128, UVR-6200, UVR-6216 of Union Carbide Corp., Danbury, CT; the Araldite GY series that is Bisphenol A epoxy liquid resins, the Araldite CT and GT series that is Bisphenol A epoxy solid resins, the Araldite GY and PY series that is Bisphenol F epoxy

liquids, the cycloaliphatic epoxides Araldite CY 179 and PY 284, the Araldite DY and RD reactive diluents series, the Araldite ECN series of epoxy cresol novolacs, the Araldite EPN series of epoxy phenol novolacs, all commercial products of Ciba Specialty Chemicals Corp., the Heloxy 48, Heloxy 44, Heloxy 84 and the other Heloxy product line, the EPON product line, all of Shell Corp., the DER series of flexible aliphatic and Bisphenol A liquid or solid epoxy resins, the DEN series of epoxy novolac resins, all commercial products of Dow Corp., Celoxide 2021, Celoxide 2021P, Celoxide 2081, Celoxide 2083, Celoxide 2085, Celoxide 2000, Celoxide 3000, Glycidole, AOEX-24, Cyclomer A200, Cyclomer M-100, Epolead GT-300, Epolead GT-302, Epolead GT-400, Epolead 401, Epolead 403, (Daicel Chemical Industries Co., Ltd.), Epicoat 828, Epicoat 812, Epicoat 872, Epicoat CT 508, (Yuka Shell Co., Ltd.), KRM-2100, KRM-2110, KRM-2199, KRM-2400, KRM-2410, KRM-2408, KRM-2490, KRM-2200, KRM-2720, KRM-2750 (Asahi Denka Kogyo Co., Ltd.).

In addition, liquid pre-reacted adducts of such epoxy resins with hardeners are suitable for use as component (A).

Cationically curable cyclic compounds other than epoxies which may be used in the compositions of the invention include oxetanes, oxolanes, cyclic acetals, anhydrides, cyclic lactones, thiiranes, and thiotanes.

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~~Typical oxetane compounds include trimethylene oxide, 3,3-dimethyloxetane and 3,3-dichloromethyloxetane, 3-ethyl-3-phenoxy-methyloxetane, and bis(3-ethyl-3-methyloxy)butane.~~

Typical oxolane compounds include tetrahydrofuran and 2,3-dimethyl-tetrahydrofuran. Typical cyclic acetal compounds include trioxane, 1,3-dioxalane and 1,3,6-trioxan cyclooctane. Typical cyclic lactone compounds include  $\beta$ -propiolactone and  $\gamma$ -butyrolactone. Typical anhydrides

include phthalic anhydride and terephthalic anhydride and hydroxy-containing derivatives thereof. Typical thiirane compounds include ethylene sulphide, 1,2-propylene sulphide and thioepichlorohydrin. Typical thiotane compounds include 1,3-propylene sulphide and 3,3-dimethylthiothane.

Vinyl ethers that can be used as a cationically polymerisable compound in the compositions of the invention include ethyl vinylether, n-propyl vinylether, isopropyl vinylether, n-butyl vinylether, isobutyl vinylether, octadecyl vinylether, cyclohexyl vinylether, butanediol divinylether, cyclohexanedimethanol divinylether, diethyleneglycol divinylether, triethyleneglycol divinylether, tert-butyl vinylether, tert-amyl vinylether, ethylhexyl vinylether, dodecyl vinylether, ethyleneglycol divinylether, ethyleneglycolbutyl vinylether, hexanediol divinylether, triethyleneglycol methylvinylether, tetraethyleneglycol divinylether, trimethylolpropane trivinylether, aminopropyl vinylether, diethylaminoethyl vinylether, ethylene glycol divinyl ether, polyalkylene glycol divinyl ether, alkyl vinyl ether and 3,4-dihydropyran-2-methyl 3,4-dihydropyran-2-carboxylate. Commercial vinyl ethers include the Pluriol-E200 divinyl ether (PEG200-DVE), poly-THF290 divinylether (PTHF290-DVE) and polyethyleneglycol-520 methyl vinylether (MPEG500-VE) all of BASF Corp.

Hydroxy-functionalised mono(poly)vinylethers include polyalkyleneglycol monovinylethers, polyalkylene alcohol-terminated polyvinylethers, butanediol monovinylether, cyclohexanedimethanol monovinylether, ethyleneglycol monovinylether, hexanediol monovinylether, diethyleneglycol monovinylether.

Another class of vinyl ethers that are suitable for inclusion in the compositions according to the invention

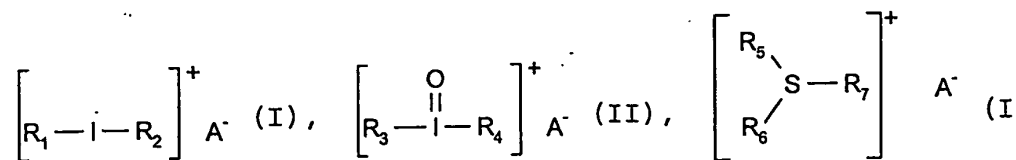
are all those included in US 5,506,087, which is incorporated herein by reference. More preferred are aromatic or alicyclic vinyl ethers. As an example, commercial vinylethers include Vectomer 4010, Vectomer 5015, Vectomer 4020, Vectomer 21010 and Vectomer 2020 of Allied Signal Corp., Morristown, NJ. Most preferred are Vectomer 4010 and Vectomer 5015.

Other cationically polymerisable compounds include spiro ortho esters that are prepared by reacting epoxy compounds with lactone; and other ethylenically unsaturated compounds, such as vinylcyclohexane, n-vinyl-2-pyrrolidone and its various derivatives, isobutylene and polybutadiene, and derivatives of the above compounds.

A mixture of two or more different cationically polymerisable compounds may be present in the composition of the invention, depending upon the intended use.

Component (B) is preferably an onium salt with an anion of weak nucleophilicity. Examples are halonium salts, iodosyl salts or sulphonium salts, for example those described in EP 153904A, sulphoxonium salts; for example those described in EP 35969A, EP 44272A, EP 54509A and EP 164314A, and diazonium salts, for example those described in US 3708296. An overview of further known onium salt initiators is offered by "UV-Curing, Science and Technology", (Editor: S.P. Pappas, Technology Marketing Corp., 642 Westover Road, Stamford, Connecticut, USA) or ~~"Chemistry & Technology of UV & EB Formulations for Coatings, Inks & Paints", Vol. 3 (edited by P. K. T. Oldring). All of these are incorporated herein by~~  
reference.

Preferred compositions comprise, as a cationic photoinitiator, a compound of the formula  
(I), (II) or (III)



II),

in which each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ , and  $R_7$  independently of one another are  $C_6$ - $C_{18}$ aryl which is unsubstituted or substituted by appropriate radicals, and

$A^-$  is  $CF_3SO_3^-$  or, preferably, an anion of the formula  $[LQ_m]^-$ , where

$L$  is boron, phosphorus, arsenic or antimony,

$Q$  is a halogen atom, or some of the radicals  $Q$  in an

anion  $LQ_m^-$  may also be hydroxyl groups, and

$m$  is an integer corresponding to the valency of  $L$  enlarged by 1.

Examples of  $C_6$ - $C_{18}$ aryl in this context are optionally substituted phenyl, naphthyl, anthryl and phenanthryl.

Suitable optional substituents include alkyl, preferably  $C_1$ - $C_6$ alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl or the various pentyl or hexyl isomers, alkoxy, preferably  $C_1$ - $C_6$ alkoxy,

such as methoxy, ethoxy, propoxy, butoxy, pentoxy or hexoxy, alkylthio, preferably  $C_1$ - $C_6$ alkylthio, such as methylthio, ethylthio, propylthio, butylthio, pentylthio or hexylthio, halogen, such as fluorine, chlorine, bromine or iodine, amino groups, cyano groups, nitro groups or

arylthio, such as phenylthio. Examples of preferred halogen atoms  $Q$  are chlorine and, in particular, fluorine. Preferred anions  $LQ_m$  are  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $SbF_6^-$  and  $SbF_5(OH)^-$ .

Particularly preferred compositions are those

comprising as a cationic photoinitiator a compound of the

formula (III), in which  $R_5$ ,  $R_6$  and  $R_7$  are aryl, aryl being in particular phenyl and/or biphenyl. Commercially available photoinitiators of this type include the bis-sulphonium antimony hexafluoro compounds UVI 6974 and UVI 5 6976.

Component (C) comprises at least one stabiliser which is a complex (sometimes referred to as a coordination compound) of a Lewis acid and a Lewis base. A Lewis acid is a substance which can accept an electron pair from a 10 base. A Lewis base is a substance which can donate an electron pair. The donated electron pair is then shared between acid and base (see for example Organic Chemistry, John McMurry, Fifth edition, p. 57-61; McGraw-Hill Encyclopedia of Science and Technology, Vol 1, p. 50-51). 15 The Lewis acid may for example be  $BX_3$ ,  $AlX_3$ ,  $FeX_3$ ,  $FeX_2$ ,  $ZnX_2$ ,  $TiX_3$  or  $TiX_4$  where each X independently represents a C(1-6)alkyl or C(1-6)alkoxy group or a hydrogen, chlorine, bromine, iodine or fluorine atom. Preferably each X is the same. Where X is an alkyl group, it is preferably an 20 ethyl group. Where X is a halogen atom, it is preferably a chlorine or fluorine atom. Preferably the Lewis acid is  $BX_3$ .

The Lewis base may for example be an amine or a phosphine. Preferred amines and phosphines include amines 25 and phosphines of the general formula



in which Z is nitrogen or phosphorus, and each  $R_8$  30 independently represents a hydrogen atom (provided that not more than two  $R_8$  groups represent hydrogen); an alkyl group having from 1 to 20, preferably from 1 to 8, especially from 1 to 4, carbon atoms, optionally substituted with one or more alkyl groups, in which the

phenyl group may be optionally substituted by one or more C(1-12) alkyl groups and/or halogen atoms) or C(5-7)cycloalkyl groups; a phenyl group optionally substituted by one or more C(1-12)alkyl groups and/or halogen atoms; 5 or a C(5-7)cycloalkyl group; or two R<sub>8</sub>'s together represent an alkylene group having from 4 to 6 carbon atoms one or more of which may be replaced by an oxygen or a sulphur atom; and in which each alkyl, cycloalkyl or phenyl group present in the compound of the formula IV may 10 be optionally substituted by one or more, preferably one or two, groups -Z(R<sub>8</sub>)<sub>2</sub>.

Preferably, each R<sub>8</sub> independently represents a C(1-12)alkyl group or a phenyl group.

Especially preferred are complexes in which the amine 15 or phosphine is a tertiary amine or tertiary phosphine. Where each X is an alkyl group, the amine or phosphine is preferably a primary or secondary amine or phosphine.

Preferably the complex is an amine complex.

Such complexes may be made by known methods and many 20 are available commercially. Particular examples of suitable complexes include the following: borane triethylamine complex; borane tributylphosphine complex; borane trimethylamine complex; borane triphenylphosphine complex; borane tributylamine complex; borane N,N- 25 diethylamine complex; borane N,N-diisopropylethylamine complex; borane dimethylamine complex; borane N-ethyl-N-isopropyl aniline complex; borane 4-methylmorpholine complex; borane 4-ethylmorpholine complex; bis-(triethylborane) 1,6-diaminohexane complex; 30 benzylaminotrifluoroborane; 2-propanaminetrifluoroborane; 4-chlorobenzylaminetrifluoroborane; and trichloroborane N,N-dimethyloctylamine complex.

Typically the complex contains one equivalent of a Lewis acid per equivalent of Lewis base, for example one



equivalent of a compound of formula  $BX_3$  per equivalent of amine or phosphine.

Component (C) of the composition according to the invention is present in an amount of from 0.001 to 0.3wt%, preferably from 0.001 to 0.1wt%. The optimal amount of component (C) present in any particular composition will depend upon the amount of cationic photoinitiator present in the composition. In general, the higher the amount of cationic photoinitiator present, the higher the amount of component (C) required to give effective stabilisation. The quantity of component (C) will however be as low as possible as excessive amounts of component (C), far from stabilising the composition, can lead to gelling or even curing of the composition.

The compositions of the present invention may also contain further components depending upon the intended use and desired properties of the compositions. For example, in addition to the cationically polymerisable compound, the compositions according to the present invention also preferably comprise a free radically curable component. This component preferably comprises at least one solid or liquid poly(meth)acrylate, for example, di-, tri-, tetra- or pentafunctional monomeric or oligomeric aliphatic, cycloaliphatic or aromatic acrylates or methacrylates. Such compounds preferably have a molecular weight of from 200 to 500.

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Examples of suitable aliphatic poly(meth)acrylates

having more than two unsaturated bonds in their molecules are the triacrylates and trimethacrylates of hexane-2,4,6-triol, glycerol or 1,1,1-trimethylolpropane, ethoxylated or propoxylated glycerol or 1,1,1-trimethylolpropane, and the hydroxyl-containing tri(meth)acrylates which are obtained by reacting triepoxide compounds, for example the

acid. It is also possible to use, for example, pentaerythritol tetraacrylate, bistrimethylolpropane tetraacrylate, pentaerythritol monohydroxytriacylate or -methacrylate, or dipentaerythritol

5 monohydroxypentaacrylate or -methacrylate.

It is additionally possible, for example, to use polyfunctional urethane acrylates or urethane methacrylates. These urethane (meth)acrylates are known to the person skilled in the art and can be prepared in a  
10 known manner by, for example, reacting a hydroxyl-terminated polyurethane with acrylic acid or methacrylic acid, or by reacting an isocyanate-terminated prepolymer with hydroxyalkyl (meth)acrylates to give the urethane (meth)acrylate.

15 Examples of suitable aromatic tri(meth)acrylates are the reaction products of triglycidyl ethers of trihydric phenols and phenol or cresol novolaks containing three hydroxyl groups, with (meth)acrylic acid.

The (meth)acrylates used herein are known compounds  
20 and some are commercially available, for example from the SARTOMER Company under product designations such as SR<sup>®</sup>295, SR<sup>®</sup>350, SR<sup>®</sup>351, SR<sup>®</sup>367, SR<sup>®</sup>399, SR<sup>®</sup>444, SR<sup>®</sup>454 or SR<sup>®</sup>9041.

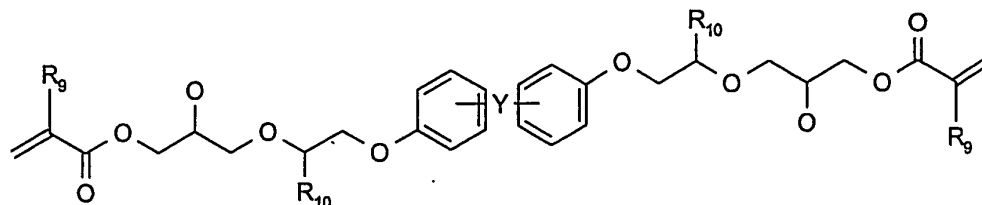
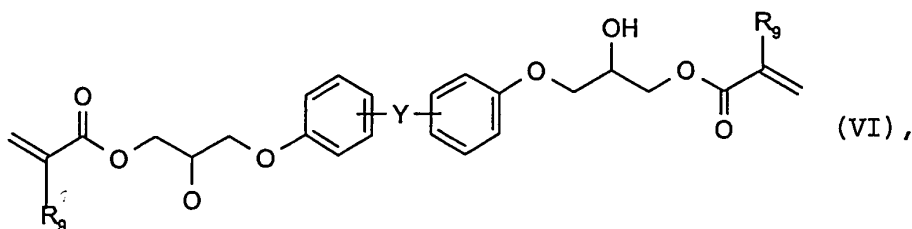
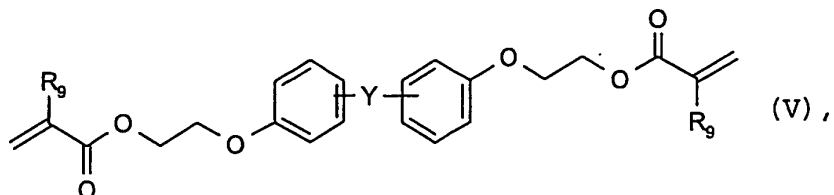
Preferred compositions are those in which the free  
25 radically curable component contains a tri(meth)acrylate or a penta(meth)acrylate.

Suitable examples of di(meth)acrylates are the di(meth)acrylates of cycloaliphatic or aromatic diols such as 1,4-dihydroxymethylcyclohexane, 2,2-bis(4-hydroxy-  
30 cyclohexyl)propane, bis(4-hydroxycyclohexyl)methane, hydroquinone, 4,4'-dihydroxybi-phenyl, Bisphenol A, Bisphenol F, bisphenol S, ethoxylated or propoxylated Bisphenol A, ethoxylated or propoxylated Bisphenol F or

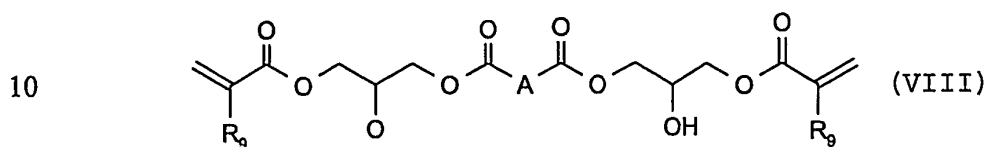
ethoxylated or propoxylated bisphenol S.

Di(meth)acrylates of this kind are known and some are commercially available.

Other di(meth)acrylates which can be employed are 5 compounds of the formulae (V), (VI), (VII) or (VIII)



(VII),



10

in which

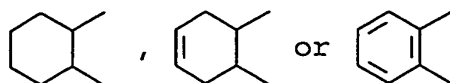
~~R<sub>9</sub> is a hydrogen atom or methyl,~~

Y is a direct bond, C<sub>1</sub>-C<sub>6</sub>alkylene, -S-, -O-, -SO-, -SO<sub>2</sub>- or -CO-,

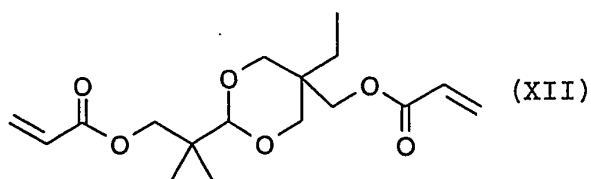
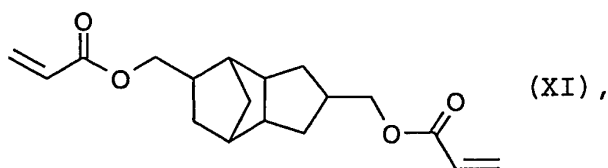
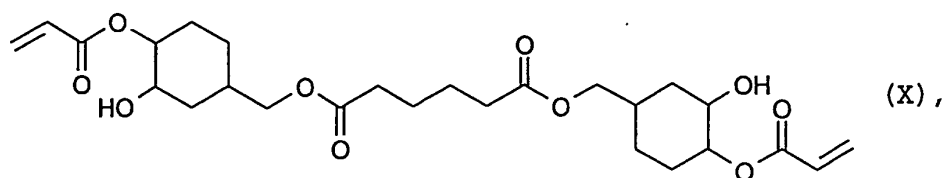
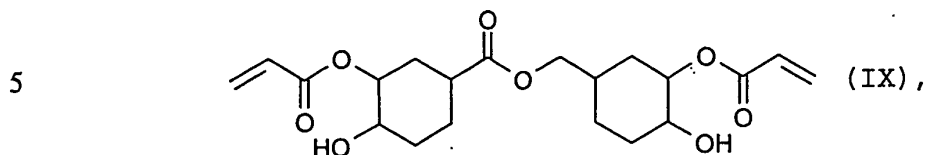
15 R<sub>10</sub> is a C<sub>1</sub>-C<sub>8</sub>alkyl group, a phenyl group which is unsubstituted or substituted by one or more C<sub>1</sub>-C<sub>4</sub>alkyl groups, hydroxyl groups or halogen atoms, or is a radical of the formula -CH<sub>2</sub>-CR<sub>11</sub> in which

R<sub>11</sub> is a C<sub>1</sub>-C<sub>4</sub>alkyl group or alkyl group and

A is an alkylene group or a group of the formula



Further examples of possible di(meth)acrylates are compounds of the formulae (IX), (X), (XI) and (XII)



These compounds of the formulae (V) to (XII) are known and some are commercially available. Their preparation is also described in EP-A-0 646 580.

Examples of commercially available products of these polyfunctional monomers are KAYARAD R-526, HDDA, NPGDA, TPGDA, MANDA, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, THE-330, DPHA-2H, DPHA-2C, DPHA-21, D-310, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, TPA-320, TPA-330, RP-1040, R-011, R-300, R-205 (Nippon Kayaku Co., Ltd.), Aronix M-210, M-220,

M-233, M-240, M-215, M- 305, M-309, M-310, M-315, M-325,  
M-400, M-6200, M-6400 (Toagosei Chemical Industry Co,  
Ltd.), Light acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA, DCP-  
A (Kyo-eisha Chemical Industry Co., Ltd.), New Frontier  
5 BPE-4, TEICA, BR-42M, GX-8345 (Daichi Kogyo Seiyaku Co.,  
Ltd.), ASF-400 (Nippon Steel Chemical Co.), Ripoxy SP-  
1506, SP-1507, SP-1509, VR-77, SP-4010, SP-4060 (Showa  
Highpolymer Co., Ltd.), NK Ester A-BPE-4 (Shin-Nakamura  
Chemical Industry Co., Ltd.), SA-1002 (Mitsubishi Chemical  
10 Co., Ltd.), Viscoat-195, Viscoat-230, Viscoat-260,  
Viscoat-310, Viscoat-214HP, Viscoat-295, Viscoat-300,  
Viscoat-360, Viscoat-GPT, Viscoat-400, Viscoat-700,  
Viscoat-540, Viscoat-3000, Viscoat-3700 (Osaka Organic  
Chemical Industry Co., Ltd.).

15 If the composition according to the present invention  
also comprises a free radically curable component it  
should also contain at least one free radical initiator.  
It is possible to employ all types of photoinitiators  
which form free radicals given the appropriate  
20 irradiation. Typical representatives of free-radical  
photoinitiators are benzoin, such as benzoin, benzoin  
ethers, such as benzoin methyl ether, benzoin ethyl ether  
and benzoin isopropyl ether, benzoin phenyl ether and  
benzoin acetate, acetophenones, such as acetophenone, 2,2-  
25 dimethoxy-acetophenone and 1,1-dichloroacetophenone,  
benzil, benzil ketals, such as benzil dimethylketal and  
~~benzil diethyl ketal, anthraquinones, such as 2-~~  
methylantraquinone, 2-ethylantraquinone, 2-tert-  
butylantraquinone, 1-chloroanthraquinone and 2-  
30 amylantraquinone, and also triphenylphosphine,  
benzoylphosphine oxides, for example 2,4,6-  
trimethylbenzoyl-diphenylphosphine oxide (Luzirin® TPO),  
bisacylphosphine oxides, benzophenones, such as

benzophenone and 4,4'-bis(N,N'-dimethylamino)benzophenone, thioxanthenes and xanthenes, acridine derivatives, phenazine derivatives, quinoxaline derivatives or 1-phenyl-1,2-propanedione 2-O-benzoyl oxime, 1-aminophenyl  
5 ketones or 1-hydroxy phenyl ketones, such as 1-hydroxy-cyclohexyl phenyl ketone, phenyl 1-hydroxyisopropyl ketone and 4-isopropylphenyl 1-hydroxyisopropyl ketone, all of which constitute known compounds. A particularly preferred free radical initiator is IR 184, available from  
10 Ciba Geigy, which is phenyl 1-hydroxycyclohexyl ketone.

Preferably a composition according to the invention comprises from 20 to 60wt% of an cationically polymerisable compound; from 0.1 to 10wt% of cationic initiator; from 5 to 40wt% of a radically curable  
15 component; from 0.1 to 10% of a radical initiator; and from 0.001 to 0.3wt% of a stabiliser which is a complex of a Lewis acid with a Lewis base.

The compositions according to the invention may also advantageously contain hydroxy compounds, for example as  
20 described in US 6379866, US 5629133 and US 5972563, for example hydroxy terminated polyethers, such as polytetrahydrofuran diols and polyols having a molecular weight of about 250 to about 4000, or siloxane/polyethylene oxide copolymers.

25 The present invention is useful for the stabilisation of compositions such as those described in US 5476748, the contents of which are incorporated herein by reference. Accordingly, in a preferred embodiment of the invention, there is provided a composition comprising

30

a) from 40 to 80% by weight of at least one liquid epoxy resin having an epoxy functionality of equal to or greater than 2,

b) from 0.1 to 10% by weight of at least one cationic photoinitiator for component a),

c) from 5 to 40% by weight of at least one liquid diacrylate,

5 d) from 0 to 15% by weight of at least one liquid poly(meth-)acrylate having a (meth-)acrylate functionality of greater than 2, the proportion of component d) preferably constituting a maximum of 50% by weight of the total (meth-)acrylate content,

10 e) from 0.1 to 10% by weight of at least one radical photoinitiator for component c) and, where appropriate, d),

f) from 5 to 40% by weight of at least one OH-terminated polyether, polyester or polyurethane, and

15 g) at least one stabiliser which is a complex of a Lewis acid and a Lewis base, component (g) being present in the composition in an amount of from 0.001 to 0.3wt%.

The compositions according to the invention can further include customary additives for epoxy

20 compositions, such as colouring agents, such as pigments and dyes, antifoaming agents, leveling agents, thickening agents, flame retardants, antioxidants and fillers such as silica, alumina, glass powder, ceramic powder and metal powder.

25 The novel compositions of the present invention can be prepared in a known manner by, for example, premixing ~~individual components and then mixing these premixes, or~~  
by mixing all of the components using customary devices, such as stirred vessels, in the absence of light and, if  
30 desired, at slightly elevated temperature. The physical form of the composition will depend upon the intended application, and may for example be a powder, a paste, or a liquid.

The novel compositions can be polymerized by irradiation with actinic radiation, for example by means of electron beams, X-rays, UV or VIS light, preferably with radiation in the wavelength range of 280-650 nm.

5 Particularly suitable are laser beams of HeCd, argon or nitrogen, metal vapour lasers, and NdYAG lasers and their frequency doubled or trebled counterparts.

The invention additionally relates to a method of producing a cured product, which comprises treating a  
10 composition according to the invention with actinic radiation. For example, it is possible in this context to use the novel compositions as adhesives, for example in DVD manufacture, as coating compositions, as photoresists, for example as solder resists, for rapid prototyping, for  
15 example by stereolithography or by ink jet printing, or for inkjet printing for producing visual or non-visual markings on any substrates. The present invention is particularly useful in the field of compositions for use in stereolithography. The requirements for compositions  
20 for use in this field are challenging. Liquid compositions for stereolithography usually have a low viscosity, but because the compositions generally contain an initiator which generates a strong acid, maintaining this low viscosity on storage is difficult. Where the  
25 stereolithography composition is a paste, control of viscosity is also very important and premature curing can be a major problem. The present invention is also particularly useful in the field of inkjet printing. Here, jetting of the composition is often carried out at  
30 elevated temperature, and premature gelling or thickening of the printing composition can be a particular problem, leading to blockage of the printing jets. It is an advantage of the present invention that stabilisation is obtained not only at room temperature or below, but also



at elevated temperatures, for example those used during inkjet printing, typically around 65°C.

When the novel compositions according to the invention are employed as coating compositions, the resulting coatings on wood, paper, metal, ceramic, glass, or other surfaces are clear and hard. The coating thickness may vary greatly and can for instance be from 0.01 mm to about 1 mm. Specific coating applications include the coating of optical fibres, and the production of marine coatings. Using the novel compositions it is possible to produce relief images for printed circuits or printing plates directly by irradiation of the mixtures, for example by means of a computer-controlled laser beam of appropriate wavelength or employing a photomask and an appropriate light source. Alternatively, the compositions may be printed using piezo ink jet technology directly onto printing plates or circuit boards, and cured by overall or selective irradiation.

The invention further provides the use of a complex of a Lewis acid and a Lewis base as a stabiliser for a composition containing at least one actinic radiation curable, cationic ring opening compound and at least one cationic photoinitiator for said cationically polymerisable compound.

25

The following Examples illustrate the invention.

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The use of boron trichloride/dimethyloctylamine complex (DY9577, from Vantico Ltd) as a viscosity stabiliser in cationic formulations is exemplified, and compared to the resin without stabiliser.

Example 1

180 g of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (Uvacure 1500, manufactured by Dow Chemicals) was mixed with 20 g of mixed triarylsulfonium hexafluoroantimonate salts in 50% by weight propylene carbonate (Cyracure 6976, supplied by Dow Chemicals). This liquid composition 1 was then used in examples 2-5.

10 Example 2

To 20 g of liquid composition 1 was added 4.1 mg of DY9577 (MW = 275.15g/mol) in a brown Nalgene bottle. The mixture was stirred on a roller mixer for 5 hours at room temperature. In Example 2, the liquid composition 1 contains 204 parts per million of DY9577 (0.0204 wt%; 0.74 mmol per kilogram of resin).

Examples 3 and 4

Mixtures characterised by the compositions listed in table 1 were prepared as in example 2. The quantitative data in table 1 are wt%. For comparison purposes, the amount of stabiliser is also given in mmol per kilogram of resin (mmol/kg).

25 Table 1

Example No.	DY9577 wt% (mmol/kg)
3	0.041 (1.49)
4	0.055 (2.00)

Liquid composition 1 and examples 2 to 4 (contained in sealed, brown Nalgene bottles) were placed in an oven at 65°C to perform accelerated ageing. The viscosity was measured every 2-3 days (Brookfield DVII2, HB, cone and plate, Spindle S40, 10rpm). Viscosities at 25°C (mPa.s) are reported in table 2. Liquid composition 1 was chosen as a general cationic photocurable composition to demonstrate the stabilising effect of DY9577. Accelerated ageing at 65°C reveals how stable/unstable a liquid composition can be upon storage. When applied to kinetically controlled reaction rates, the Arrhenius equation predicts that a 10°C increase in temperature will double the reaction rate. A 2-week stability test at 65°C is equivalent to over 7 months storage at 25°C.

Table 2

day	0	3	9
Liquid composition 1 (comparison)	238	311	24300
Example 2	238	320	1000
Example 3	238	299	880
Example 4	238	294	820

~~As shown here, when used in small amounts, far from~~  
 initiating the polymerisation of the epoxies, DY9577 slows  
 down significantly the ageing process of the cycloaliphatic epoxy in the presence of a cationic photoinitiator at 65°C. This is a most unusual result, as DY9577 is a latent thermal catalyst for epoxies.

### Example 5

The liquid composition 2 described in Table 3 was the base for experiments performed to assess the performance of DY9577 as a viscosity stabiliser in a typical 5 photocurable composition used in stereolithography.

Table 3

Class of compound	Commercial name	Manufacturer	Wt %
Cycloaliphatic epoxide	Uvacure 1500	Dow Chemicals	48.5
Glycidyl ethers	Heloxyl 48	Resolution	11 (
	Heloxyl 84	Resolution	6.1 (
Acrylates	SR399	Sartomer	6.1 (
	Ebecryl 3700	UCB chemicals	6.3
polyol	Terathane 1000	Du Pont	15.0
Free-radical Photoinitiator	Irgacure 184	Ciba SC	2.0
Cationic Photoinitiator	Cyracure 6976	Dow	5.0

The components were stirred at 60°C until a clear 10 homogeneous mixture formed.

### Example 6

To 31.1 g of liquid composition 2 was added 6.3 mg of DY9577 (MW = 275.15 g/mol) in a brown nalgene bottle. The 15 mixture was stirred on a roller mixer for 5 hours at room temperature. In Example 6, the liquid composition 2 contains 203 parties per million of DY9577 (0.0203 wt%; 0.74 mmol per kilogram of resin).

Examples 7-17

Mixtures characterised by the compositions listed in table 2 were prepared as in example 6. The quantitative data in table 4 are weight percent (wt%). For comparison purposes, the amount of stabiliser is also given in mmol per kilogram of resin (mmol/kg).

Table 4

Example No.	DY9577
	wt% (mmol/kg)
7	0.0407 (1.48)
8	0.0548 (1.99)
9	0.0680 (2.47)
10	0.0800 (2.91)
11	0.0961 (3.49)
12	0.108 (3.94)
13	0.152 (5.52)
14	0.200 (7.26)
15	0.300 (10.89)
16	0.499 (18.14)
(comparison)	
17	1.000 (36.31)
(comparison)	

10

The photospeed of the compositions listed in table 4 were determined using methods well known in the art, using a SLA apparatus (SLA 7000 3D-Systems). Depth of Penetration (Dp, in mils) and Critical Exposure (Ec, in mW/cm<sup>2</sup>) are given in table 5. Also listed are E4 and E11, the energies respectively needed to cure layers of 4 and 11 mls of thickness.

Table 5

Composition	Dp (mls)	Ec (mW/cm <sup>2</sup> )	E4 (mW/cm <sup>2</sup> )	E11 (mW/cm <sup>2</sup> )
Liquid composition 2 (comparison)	5.09	7.43	16.31	64.591
Example 6	4.87	6.95	15.796	66.425
Example 7	5.13	7.77	16.954	66.387
Example 8	5.19	7.82	16.891	65.043
Example 9	4.88	6.73	15.293	64.251
Example 10	5.11	7.56	16.531	65.070
Example 11	5.02	7.43	16.488	66.561
Example 12	5.05	7.65	16.882	67.534
Example 13	4.94	7.08	15.921	65.731
Example 14	4.97	7.27	16.242	66.372
Example 15	4.94	7.10	15.961	65.889

The data gathered in Table 5 show that the boron-amine complex does not significantly affect the photospeed of the stereolithography resin. This is a crucial result. Due to their basic character viscosity stabilisers are expected to reduce the photospeed of UV-curable resins. Finding a viscosity stabiliser that will capture the acid species created upon ageing without affecting the cure properties of the resin is a real breakthrough.

#### Example 18

Thermal ageing at 65°C was been performed on the compositions of examples 6-17. Samples were placed in sealed brown Nalgene bottles at 65°C. The viscosities measured every 2-3 days are reported in table 6.

## Table 6

[illegible]

The accelerated ageing at 65°C shows very clearly that small amounts of DY9577 are very effective at slowing down the ageing process of liquid composition 2. Without any stabiliser, the resin gels after 11 days at 65°C, whereas small amounts of DY9577 increases its storage stability, slowing down the ageing process and deferring the gelling time. However, increasing the amount of DY9577 represents a danger, as shown in comparative examples 16 and 17, containing 0.5 and 1.0 wt% of the stabiliser. At these levels, DY9577 does not act as a stabiliser any longer, but acts as a thermal catalyst and induces gelling within a day.

#### Example 19-21

Green flexural modulus (GFM) of liquid composition 2, example 7 and example 9 were measured. 150g of resin were placed in a small tub and 3 flexural bars (2.66 x 6.23 x 40 mm) were built with a SLA 7000 (3D-Systems). The flexural modulus at 1mm deflection is measured 10 min and 1 hour after the end of the build. The 3rd bar is kept for 48 hours at 25°C, 50% relative humidity, and UV-cured for 90 min in a PCA oven. The green flexural modulus in MPa after 10 min, 1hour, and after UV-curing are given in table 7.

Table 7

	10min-GFM	1h-GFM	UV-cured
Liquid composition 2	17	85	1430
Example 7	19	84	1470
Example 9	14	78	1460



This example demonstrates that DY9577 used in an appropriate amount does not affect the green strength of a stereolithography part. Green strength is a major property in stereolithography: the parts built by this process must be strong enough to stand without collapsing under their own weight and to be removed from the metallic platform on which they have been built without damage. DY9577 does not affect the photospeed, the green strength or the final flexural modulus of the cured material, as compared to the non-modified resin, and does increase the storage stability of the liquid resin.

#### Example 22

The liquid composition 3 described in Table 8 is used in a test designed to mimic the formation of free acid in a vat in a SLA apparatus. The viscosity of the liquid composition 3 is 380 mPa.s at 25°C, and the epoxy value is 5.86 mol/kg.

Table 8

Class of compound	Commercial name	Manufacturer	wt %
Cycloaliphatic epoxide	Uvacure 1500	Dow Chemicals	50.2
Glycidyl ethers	Heloxyl 48	Resolution	30.0
Acrylates	SR399	Sartomer	6.2
	Ebecryl 3700	UCB chemicals	6.3
Free-radical Photoinitiator	Irgacure 184	Ciba SC	2.5
Cationic Photoinitiator	Cyracure 6976	Dow	5.0

437g of liquid composition 3 are placed in a small plastic tub. A 3-dimension part made of fine supports, referred to as the "sponge part" is build with a SLA 7000 (3D-Systems). Ideally, the part occupies the largest possible volume of the small tub of resin. When building the fine part, the laser will also slightly irradiate the surrounding liquid resin thus producing unwanted acid species that can start polymerising the epoxy monomers.

The fine structure of the test part is designed to amplify this effect resulting in increased viscosity. In total, three sponge parts are built in the same resin, at 24 hour intervals, and the viscosity of the resin is measured just before the following test (23 hours after the end of the previous build), after draining the previous test part (Table 9). Epoxy values are also to confirm that the increased viscosity is due to the uncontrolled polymerisation of the epoxide monomers (decreasing epoxy value after several sponge tests).

20

Table 9

	Viscosity at 25°C (mPa.s)	Epoxy value (mol/kg)
Before test	380	5.86
23h after 1 sponge	460 (+21%)	5.78
23 h after 2 sponges	680 (+79%)	5.65
23h after 3 sponges	1375 (+262%)	5.58

Example 23

To 471.7 g of liquid composition 3 were added 373 mg of DY9577 (0.079 wt%; 2.87mmol/kg). The mixture was stirred for 1hour before 437 g were placed in a tub and the experiment described in example 25 was repeated. The results are reported in Table 10.

Table 10

	Viscosity at 25°C (mPa.s)	Epoxy value (mol/kg)
Before test	380	5.86
23h after 1 sponge	400-415 (+5-9%)	
23 h after 2 sponges	500-525 (+31-38%)	
23h after 3 sponges	580 (+53%)	5.75

Examples 22 and 23 show the remarkable effect of DY9577 as a viscosity stabiliser. The increase in viscosity for the resin stabilised with 0.079 wt% of DY9577 is much less dramatic than the original resin. The decrease in the epoxy value further demonstrates that the viscosity rise is due to the gelling of the epoxides.

Claims

1. An actinic radiation curable composition comprising:
- 5 (A) at least one actinic radiation curable, cationically polymerisable compound;
- (B) at least one cationic photoinitiator for component (A); and
- 10 (C) at least one stabiliser which is a complex of a Lewis acid and a Lewis base, component (C) being present in the composition in an amount of from 0.001 to 0.3wt%.
2. A composition as claimed in claim 1, in which the
- 15 Lewis acid of component (C) is selected from  $BX_3$ ,  $AlX_3$ ,  $FeX_3$ ,  $FeX_2$ ,  $ZnX_2$ ,  $TiX_3$  or  $TiX_4$  where each X independently represents a C(1-6)alkyl or C(1-6)alkoxy group or a hydrogen, chlorine, bromine, iodine or fluorine atom.
- 20 3. A composition as claimed in claim 2, in which the Lewis acid of component (C) is  $BX_3$ .
4. A composition as claimed in any one of claims 1 to 3, in which the Lewis base of component (C) is an amine or a
- 25 phosphine.
5. A composition as claimed in claim 4, in which the Lewis base of component (C) is an amine or a phosphine of the general formula

30



in which Z is nitrogen or phosphorus, and each  $R_8$  independently represents a hydrogen atom (provided that

not more than two  $R_8$  groups represent hydrogen); an alkyl group having from 1 to 20, preferably from 1 to 8, especially from 1 to 4, carbon atoms, optionally substituted by one or more phenyl groups (in which the phenyl group may be optionally substituted by one or more C(1-12)alkyl groups and/or halogen atoms) or C(5-7)cycloalkyl groups; a phenyl group optionally substituted by one or more C(1-12)alkyl groups and/or halogen atoms; or a C(5-7)cycloalkyl group; or two  $R_8$ 's together represent an alkylene group having from 4 to 6 carbon atoms one or more of which may be replaced by an oxygen or a sulphur atom; and in which each alkyl, cycloalkyl or phenyl group present in the compound of the formula IV may be optionally substituted by one or more, preferably one or two, groups  $-Z(R_8)_2$ .

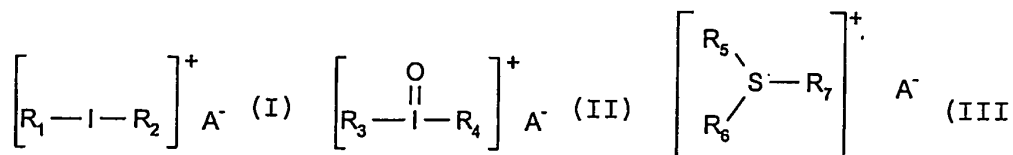
6. A composition as claimed in claim 5, in which each  $R_8$  independently represents a C(1-12)alkyl group or a phenyl group.

20

7. A composition as claimed in claim 1, in which component (C) is selected from the group consisting of borane triethylamine complex; borane tributylphosphine complex; borane trimethylamine complex; borane triphenylphosphine complex; borane tributylamine complex; borane N,N-diethylamine complex; borane N,N-diisopropylethylamine complex; borane dimethylamine complex; borane N-ethyl-N-isopropyl aniline complex; borane 4-methylmorpholine complex; borane 4-ethylmorpholine complex; bis-(triethylborane) 1,6-diaminohexane complex; benzylaminotrifluoroborane; 2-propanaminetrifluoroborane; 4-chlorobenzylaminetrifluoroborane; and trichloroborane N,N-dimethyloctylamine complex.

8. A composition as claimed in claim 7, in which component (C) is bis-(triethylborane) 1,6-diaminohexane complex or trichloroborane N,N-dimethyloctylamine complex.
- 5 9. A composition as claimed in any one of claims 1 to 8, in which component (A) includes an epoxy compound.
10. A composition as claimed in claim 9, in which component (A) includes a cycloaliphatic diepoxide.
- 10 11. A composition as claimed in claim 10, in which the monomer purity of the cycloaliphatic diepoxide is 90% or higher.
- 15 12. A composition as claimed in either claim 10 or claim 11, in which component (A) includes one or more cycloaliphatic diepoxides selected from bis(4-hydroxycyclohexyl)methane diglycidyl ether, 2,2-bis(4-hydroxycyclohexyl)propane diglycidyl ether, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-6-methyl-cyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate, di-(3,4-epoxycyclohexylmethyl)hexanedioate, di-(3,4-epoxy-6-methyl-cyclohexylmethyl)hexanedioate, ethylenebis(3,4-epoxycyclohexanecarboxylate), ethanediol di-(3,4-epoxycyclohexylmethyl) ether and 2-(3,4-epoxycyclohexyl-5,5,3-dioxane.
- 20 13. A composition as claimed in any one of claims 1 to 30 12, in which component (B) is an onium salt with an anion of weak nucleophilicity.

14. A composition as claimed in claim 13, in which component (B) comprises an onium salt of general formula (I), (II) or (III):



- 5 in which each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ , and  $R_7$  independently of one another are  $C_6$ - $C_{18}$ aryl which is unsubstituted or substituted by appropriate radicals, and  $A^-$  is  $CF_3SO_3^-$  or an anion of the formula  $[LQ_m]^-$ , where  $L$  is boron, phosphorus, arsenic or antimony,
- 10  $Q$  is a halogen atom, or some of the radicals  $Q$  in an anion  $LQ_m^-$  may also be hydroxyl groups, and
- $m$  is an integer corresponding to the valency of  $L$  enlarged by 1.

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15. A composition as claimed in claim 14, in which component (B) is a compound of the formula (III) in which  $R_5$ ,  $R_6$  and  $R_7$  are phenyl and/or biphenyl.

- 20 16. A composition as claimed in any one of claims 1 to 15, which comprises a mixture of one or more cationically polymerisable compounds as component (A).

17. A composition as claimed in any one of claims 1 to 25 16, which also comprises one or more free radically curable substances together with a free radical initiator.

18. A composition as claimed in claim 17, which comprises at least one monomeric or oligomeric acrylate or methacrylate.

5 19. A composition as claimed in any one of claims 1 to 18, which also contains a polytetrahydrofuran diol or polyol having a molecular weight of about 250 to about 4000, or a siloxane/polyethylene oxide copolymer.

10 20. A composition as claimed in claim 1, which comprises:

a) from 40 to 80% by weight of at least one liquid epoxy resin having an epoxy functionality of equal to or greater than 2,

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b) from 0.1 to 10% by weight of at least one cationic photoinitiator for component a),

20 c) from 5 to 40% by weight of at least one liquid diacrylate,

d) from 0 to 15% by weight of at least one liquid poly(meth-)acrylate having a (meth-)acrylate functionality of greater than 2,

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e) from 0.1 to 10% by weight of at least one radical photoinitiator for component c) and, where appropriate, d),

30 f) from 5 to 40% by weight of at least one OH-terminated polyether, polyester or polyurethane, and



g) at least one stabiliser which is a complex of a Lewis acid and a Lewis base, component (g) being present in the composition in an amount of from 0.001 to 0.3wt%.

5 21. A process for producing a cured product, which comprises treating a composition according to any one of claims 1 to 20 with actinic radiation.

22. The use of a complex of a Lewis acid and a Lewis base  
10 as a stabiliser for a composition containing at least one radiation curable, cationically polymerisable compound and at least one cationic photoinitiator for said compound.

23. The use of a complex of a compound of the general  
15 formula  $BX_3$  in which each X independently represents a C(1-6)alkyl group or a hydrogen, chlorine, bromine, iodine or fluorine atom with an amine or a phosphine, as a stabiliser for a composition containing at least one radiation curable, cationically polymerisable compound and  
20 at least one cationic photoinitiator for said compound.

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Actinic Radiation Curable Compositions and their Use

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Abstract

10 Actinic radiation curable compositions comprising at least one actinic radiation curable, cationically polymerisable compound and at least one cationic photoinitiator, may be stabilised by the use of a stabiliser which is a complex of a Lewis acid and a Lewis base.

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